



# Pyrolysis characteristics of the mixture of printed circuit board scraps and coal powder



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## ABSTRACT

Thermogravimetric (TG) analysis and infrared spectroscopy were used to analyze the pyrolysis characteristics of printed circuit board scraps (PCBs), coal powder and their mixtures under nitrogen atmosphere. The experimental results show that there is a large difference between waste PCBs and coal powder in pyrolysis processing. The pyrolysis properties of the mixing samples are the result of interaction of the PCBs and coal powder, which is influenced by the content of mixture. The degree of pyrolysis and pyrolysis properties of the mixture are much better than that of the single component. The TG and the differential thermogravimetric (DTG) curves of the PCBs mixed with coal powder move towards the high-temperature zone with increasing amount of coal powder and subsequently the DTG peak also becomes wider. The Coats–Redfern integral method was used to determine the kinetic parameters of pyrolysis reaction mechanism with the different proportion of mixture. The gas of pyrolysis mainly composes of CO<sub>2</sub>, CO, H<sub>2</sub>O and some hydrocarbon. The bromide characteristic absorption peak has been detected obviously in the pyrolysis gas of PCBs. On the contrary, the absorption peak of the bromide is not obvious in pyrolysis gas of the PCBs samples adding 40% coal powder.

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## 1. Introduction

With the rapid development of the electronic industry and the updating of all kinds of electrical and electronic equipment, the electronic waste (e-waste) is exponentially increasing. The recycle of e-waste all over the world is receiving more and more attention (Nnorom and Osibanjo, 2008; Zhang and Forssberg, 1997). As a typical e-waste, printed circuit board scraps (PCBs) are becoming a hot research topic in the resourcing e-waste research field. PCBs are particularly problematic to recycle because of the heterogeneous mix of organic material, metals, and glass fiber (Hall and Williams, 2007). Although some conventional disposal methods are widely applied in e-waste recycling process, the main disadvantages of these methods are being challenged due to their poor economic and environmental effects (Kang and Schoenung, 2005). Therefore, the recycling and harmless disposal of PCBs facilitates the recycle of e-waste (Guo et al., 2010; Huang et al., 2009). Pyrolysis as a new and efficient waste disposal method with low emissions not only can recycle all the valuable metals but also can deal with organic matters in PCBs (Moltó et al., 2009; Yamane et al., 2011). Hence, some scholars are focusing on using the pyrolysis technology to dispose waste PCBs (De Marco et al., 2008; Guo et al., 2009, 2010; Jie et al., 2008; Li et al., 2010; Menad et al., 1998;

Moltó et al., 2009; Quan et al., 2010). Currently, most of research directions mainly are the pyrolysis product, pyrolysis kinetics of PCBs, and the control and removal of brominated pollutants (Balabanovich et al., 2004; Barontini et al., 2005; Chien et al., 2000; Duan et al., 2012; Gan et al., 2006; Ni et al., 2012; Peng et al., 2006; Quan et al., 2009; Sun and Lu, 2002). Meanwhile, some research on the PCBs pyrolysis under special conditions is also tried. Andersson et al. used microwave pyrolysis to recycle the organic residues (Andersson et al., 2012). The effects of molten salt on the pyrolysis of PCBs were investigated (Flandinet et al., 2012). The PCBs pyrolysis experiments under the low-vacuum were also conducted (Gan et al., 2005; Long et al., 2010; Zhou and Qiu, 2010; Zhou et al., 2011). Wang's study indicated that the pyrolysis product of PCBs change greatly in the copper-catalyzed condition (Wang et al., 2009).

Generally, PCBs contains flame retardants such as halogenated compounds, which can lead to the formation of different toxic products, such as dibenzo-p-dioxins and dibenzo-furans (Duan et al., 2012; Li et al., 2010; Menad et al., 1998). The aim of most research works is to obtain the pyrolysis oils used for fuel or chemical feedstock. However, the flowsheet obtaining chemical products and liquid or gas fuel from PCBs are complicated in fact. The flowsheet of PCBs co-pyrolysis with coal for energy recovery and the slag for metal extraction is a prior and practicable process.

Little work has been done regarding the pyrolysis of PCBs mixed with coal powder, while the similar approach in the disposal of

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municipal waste and sludge incineration have been applied intensively (Luo et al., 2010; Malkow, 2004; Xie et al., 2003). Therefore, it is necessary to investigate the pyrolysis characteristic of PCBs mixed with coal powder as a new PCB processing method. Under  $N_2$ , pyrolysis tests were conducted on waste PCBs, coal powder and their mixing samples by using a thermalgravimetric analyzer and a Fourier Transform Infrared (FTIR) Spectrometer. The effect of different mixing ratios of coal powder and waste PCBs on pyrolysis was explored in this study. The pyrolysis gas derived from of PCBs, coal sample and their mixing samples was detected by FTIR Spectrometer and the effect of adding coal powder in the solidification of harmful gas is also discussed.

## 2. Experimental

### 2.1. Sample preparation

A discarded computer motherboard was selected as the PCB test sample. Firstly the components in the motherboard such as capacitors batteries were removed then the PCB was sheared and crushed to  $-20$  mm followed by pulverizing to  $-2$  mm using an ACM-420 pulverizer. As the TG samples are very little, in order to evenly mix the samples and guarantee the representation of samples, the  $-0.25$  mm part of PCB sample is sieved as the test sample. Anthracite coal (AC) sampled from Taixi coal preparation plant in northwest China and weakly caking coal (WCC) sampled from South Africa were selected for test, then the prepared coal samples were air dried and grinded. The  $-0.25$  mm size fraction of coal powder was sieved as the test sample.

The proximate analysis data of the test samples were obtained according to Chinese Standards (GB/T 212-2008), and elemental analysis of the test samples was conducted by using Vario Micro Cube made by Elementar Analysensysteme GmbH and X-Ray Fluorescence Spectrometry (BRUKER S8 TIGER). The proximate and elemental analysis data of test samples are shown in Table 1. The mixing ratios of samples are shown in Table 2.

### 2.2. Equipment and conditions

Pyrolysis tests were carried out under nitrogen using an STA409C-DTA/DSC-TG simultaneously integrating thermal analyzer made by German NETZSCH Company. The pyrolysis gas was detected by the NICOLET Nexus 470 FTIR Spectrometer with a 10 meter gas cell and DTGS detector.

Nitrogen, at 50 ml/min, was used as the protective gas for the TG. The gas phase products were continuously swept into the FTIR gas cell using nitrogen as carrier gas with a flow rate of 100 ml/min. The coupling between TG and FTIR was via heated quartz capillary. Both FTIR gas cell and capillary were heated to 473 K during experiments to prevent deposits on the walls. Each test sample was about 20 mg (accuracy up to 0.01 mg). The heating rate was 40 K/min. FTIR spectra were continuously acquired at a resolution of  $4\text{ cm}^{-1}$  and 8 scans per second during the TG measurements. The mass loss reported in this work has an accuracy of  $\pm 1\%$ .

**Table 2**

Preparation of samples.

Number	PCBs (%)	WCC (%)	AC (%)
1	100	0	
2	80	20	
3	60	40	
4	40	60	
5	20	80	
6	80		20
7	60		40
8	40		60
9	20		80
10		100	
11			100

## 3. Results and discussion

### 3.1. Single pyrolysis characteristics of the PCBs and coal powder sample

Fig. 1 shows the TG and DTG curves of the three samples. It can be seen that an inflection point is in the TG curve of PCBs sample, which corresponds to the DTG curve with a very steep single peak at  $358^\circ\text{C}$ . The maximum weight loss rate is  $-12.0\%/min$  and the main stage of pyrolysis weight loss is in the range of  $280\text{--}450^\circ\text{C}$ . During this stage, a large number of volatile is devolatilized and about 20% weight of the sample decomposes. After  $500^\circ\text{C}$ , the TG curve is relatively flat, while the PCBs sample decomposes slowly in this stage. The final residue of the sample is about 65%, which is coincident with the result of proximate analysis of the PCBs sample. It indicates that the volatile of sample has decomposed completely.

The TG and DTG curves of WCC and AC samples nearly have the same trends. The main pyrolysis temperature of WCC is in the range of  $400\text{--}900^\circ\text{C}$  and the maximum weight loss temperature is at  $490^\circ\text{C}$  with the maximum weight loss rate  $-3.3\%/min$ . The main pyrolysis stage of AC sample is in the range of  $540\text{--}885^\circ\text{C}$ . The maximum weight loss temperature is at  $680^\circ\text{C}$  with the maximum weight loss rate is  $-1.0\%/min$ . The final pyrolysis solid residues are 69% and 90%, respectively.

It can be seen in Fig. 1 that the TG and DTG curves of WCC are on the bottom of left side of the AC sample. This is coincident with results of the proximate analysis that the volatile of WCC is greater than AC. To compare the TG and DTG curves of WCC, AC and PCBs samples, the maximum weight loss peak reduces obviously, and the whole curve moves toward the high temperature zone. The temperature hysteresis causes the initial reaction temperature and the temperature corresponding with the maximum weight loss rate  $dW/dt$  and the terminal reaction temperature increase proportionately. It indicates the great difference in pyrolysis between the PCBs and coal powder samples.

### 3.2. Pyrolysis characteristics of samples mixing PCBs and coal powder

Figs. 2 and 3 present the TG and DTG curves of mixing samples of PCBs, WCC and AC. It can be seen that the main weight loss stage

**Table 1**

Proximate and elemental analysis of samples.

Sample	Proximate analysis (%)				Elemental analysis (%)					Net calorific value (MJ/kg)
	$M_{ad}$	$A_{ad}$	$V_{ad}$	$FC_{ad}$	N	C	H	S	Br	
PCBs	0.20	68.31	27.79	3.70	0.46	38.44	4.36	0.24	5.20	11.56
WCC	2.49	23.74	28.01	45.76	2.56	75.00	4.71	0.78	–	26.80
AC	0.35	5.49	7.90	86.26	1.08	86.1	3.42	0.34	–	33.89

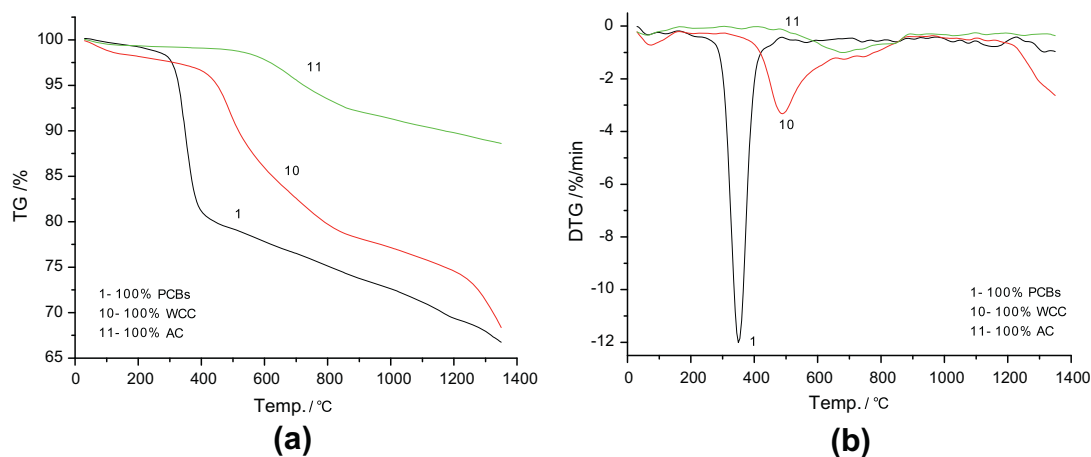


Fig. 1. TG (a) and DTG (b) curves of pyrolysis for the three single samples.

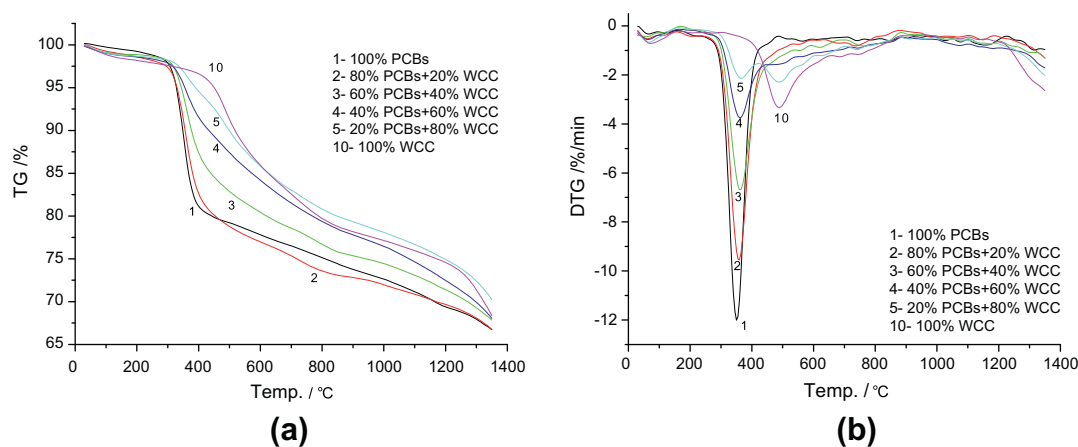


Fig. 2. TG (a) and DTG (b) curves of pyrolysis for PCBs and WCC.

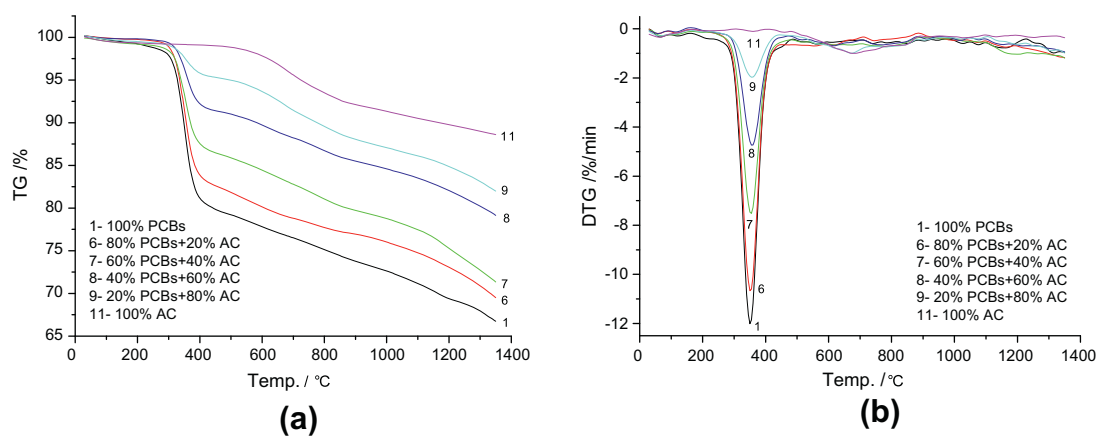


Fig. 3. TG (a) and DTG (b) curves of pyrolysis for PCBs and AC.

of the mixed sample of PCBs and AC is in the range of 300–450 °C and the mixing sample of PCBs and WCC is in the range of 250–430 °C, while the curves after that are gradual, which indicates that the mixed sample pyrolyzes slowly.

It can be seen from the TG curves that the residue of mixed pyrolysis varies with the content of PCBs increasing. The TG curves

of the PCBs sample mixed with WCC change obviously and the proportion of WCC has an effect on the amount of residue. The TG curves of the PCBs sample mixing AC change regularly and the residue decrease with increasing PCBs. It is indicated that the degree of pyrolysis for the PCBs sample is improved by adding AC to some extent, while is marginally affected by adding WCC.

The DTG curve shows that the mixed pyrolysis is more complex in the main stage of 250–500 °C. The maximum of loss rate increases coupled with the PCBs increasing. The peak of DTG is being sharp-cut. The DTG peak of single PCBs sample is narrow while the mixed pyrolysis peak is wide, the peak moves to the high-temperature zone and the temperature of maximum loss rate also turns to the high-temperature zone. This shows that the pyrolysis of PCBs mainly happens in the low-temperature zone, while the pyrolysis of mixing sample is much more uniform in the distribution of time.

The mixed pyrolysis curves of PCBs and coal powder shows that the degree of pyrolysis has been adjusted. The combined pyrolysis is much more uniform in the distribution of time. It can be concluded that the mixed pyrolysis of PCBs and coal powder is better than single pyrolysis of PCBs.

### 3.3. The reaction kinetics of pyrolysis

Thermogravimetric data was used to characterize the e-waste, municipal solid waste, and waste plastics, as well as to investigate the kinetics of the reaction that results from thermal degradation (Kantarelis et al., 2011; Liu et al., 2009; Sait et al., 2012; Zabanitoul et al., 2008). Pyrolysis is generally a complex process and it is difficult to discover kinetic models that explain the mechanism of thermal decomposition. In many of kinetic formulations of solid state reactions, it has been assumed that the isothermal homogeneous gas or liquid phase kinetic equation can be applied. Generally for e-waste degradation, it has been assumed that the rates of conversion are proportional to the concentration of reacted material (Kantarelis et al., 2011; Quan et al., 2009). In this case, some decomposition can be divided into several stages, and each stage can be described by a model of independent reactions. The overall rate of reactions is commonly described by the following equation (Aboulkas et al., 2010):

$$\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT} = K(T)f(\alpha) \quad (1)$$

where  $\alpha$  is the normalized conversion of sample's decomposition,  $\beta$  is the constant heating rate,  $f(\alpha)$  and  $K(T)$  are the functions of conversion and temperature, respectively.  $f(\alpha)$  depends on the mechanism of the thermal decomposition.

Normalized conversion is defined as:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f} \quad (2)$$

where  $m_0$  is the initial mass sample,  $m_t$  is the mass sample at time  $t$  and  $m_f$  is the mass sample at infinite time. All of the masses are on dry basis.

$K(T)$  the temperature dependence of the rate of weight loss, is often modeled successfully by the Arrhenius equation.

$$K(T) = A \exp\left(-\frac{E}{RT}\right) \quad (3)$$

where  $E$  is the activation energy,  $A$  is the pre-exponential factor and  $R$  is the gas constant.

The function  $f(\alpha)$  is dependent on the assumed reaction mechanism. However, it is often used in the form analogous to the solid waste reactions kinetics. The solid fuel pyrolysis reaction can be simulated using an  $n$ -level reaction model:

$$f(\alpha) = (1 - \alpha)^n \quad (4)$$

By combining Eqs. (1), (3), and (5), the reaction rate can be written in the form:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) (1 - \alpha)^n \quad (5)$$

Integrating this gives:

$$\int_0^\alpha \frac{d\alpha}{(1 - \alpha)^n} = \frac{A}{\beta} \int_0^T \exp\left(-\frac{E}{RT}\right) dT \quad (6)$$

The logarithm of Eq. (5) gives, when  $n$  is 1:

$$\ln \left[ \frac{-\ln(1 - \alpha)}{T^2} \right] = \ln \left[ \frac{AR}{\beta E} \left( 1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT} \quad (7)$$

When  $n$  is not 1, then we get:

$$\ln \left[ \frac{1 - (1 - \alpha)^{1-n}}{T^2(1 - n)} \right] = \ln \left[ \frac{AR}{\beta E} \left( 1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT} \quad (8)$$

Eqs. (7) and (8) are called the Coats–Redfern Equations (Hu and Shi, 2001). The method of Coats–Redfern is adopted to solve the kinetics parameter of pyrolysis reaction in this paper.

For the common pyrolysis temperatures and the most observed  $E$  values,  $\frac{E}{RT} \gg 1$  and  $(1 - \frac{2RT}{E}) \approx 1$ , so the right of Eqs. (7) and (8) in the first part are almost a constant. When  $n \neq 1$ ,  $\ln \left[ \frac{1 - (1 - \alpha)^{1-n}}{T^2(1 - n)} \right]$  map/ $T$ , and  $n = 1$ , plotting  $1/T$  versus  $\ln \left[ \frac{-\ln(1 - \alpha)}{T^2} \right]$  all gives a straight line with the slope  $-\frac{E}{R}$  for the correct value of  $n$ .

Eqs. (7) and (8) can be reduced to  $Y = a + bX$ , where  $X$  is  $1/T$ . By trying different  $n$  values, we estimate the proper  $n$ , until the resulting curve is a straight line. The value for  $a$  can be obtained at the intercept.

The pyrolysis parameters of PCBs, coal powder and their mixing samples at heating rates of 40 K/min are calculated by the method of Coats–Redfern and shown in Table 3.

Table 3 shows that the kinetic parameters of Nos. 1–11 samples are much more different. It indicates the complexity of thermogravimetric process of the mixed samples. The single pyrolyses of PCBs and AC are one-step reaction, and the thermogravimetric process of WCC reacts in several steps. From Table 3 we can see that the reaction order of sample 3 is 2.22, the highest one, but it is a one-step reaction. The reason may be that the WCC has a low fraction and the PCBs play a leading role in mixed pyrolysis.

The pyrolysis processes of other mixed samples have two or three reaction steps. This shows that the mixture of PCBs and coal powder makes the thermogravimetric process much more complex and the reaction orders are 1–2. With the increase of coal powder proportion, the activity energy decreases, which benefits to the pyrolysis reaction. From the correlation coefficient  $R$ , we know that the first step of reaction is suitable. It shows that the thermal kinetic function which is calculated by the method of Coats–Redfern can forecast the degree of pyrolysis reaction of the mixed samples with the PCBs and coal powder well.

It is found that during pyrolysis process, values of activation energy ( $E$ ) changed with different samples. For PCBs sample, the  $E$  value is 205 kJ mol<sup>−1</sup>. The  $E$  values of PCBs added WCC coal powder range from 42.4 kJ mol<sup>−1</sup> to 213 kJ mol<sup>−1</sup>, while the range of  $E$  is 19.6–190 kJ mol<sup>−1</sup>. Most activation energy values during pyrolysis decrease after adding coal powder. With a comparison on literature sources subjected to N<sub>2</sub> atmosphere, while the products released during the first phase were mainly H<sub>2</sub>O and CO<sub>2</sub>, the flame retardants and other plastic additives were decomposed or volatilized, releasing small-molecule products within the second phase, including HBr, H<sub>2</sub>O, CO<sub>2</sub> and molecular hydrocarbons (Li et al., 2010). It is indicated that complete pyrolysis and carbonization occurred during the last phase.

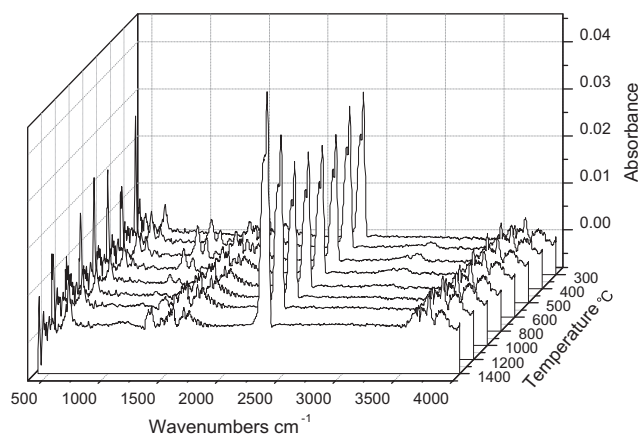
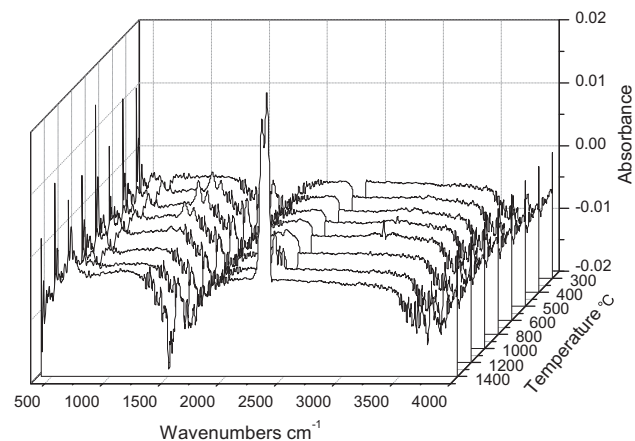
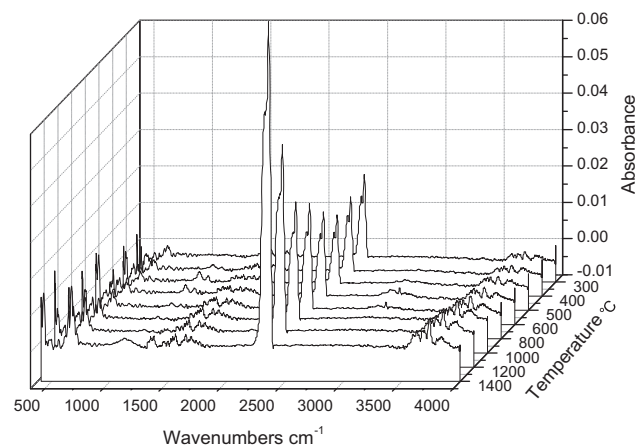
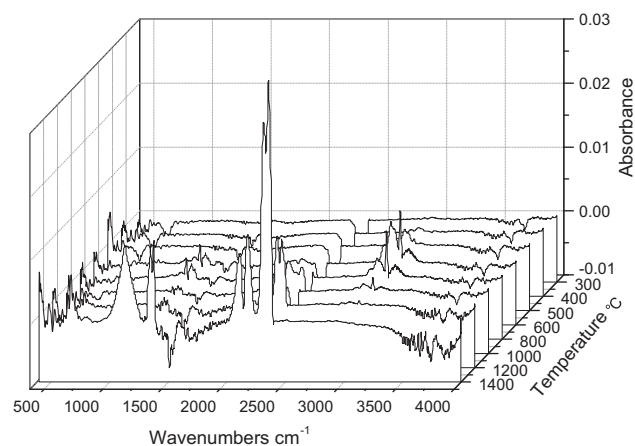
### 3.4. FTIR analysis

FTIR spectrum is used to analyze the gas produced in the pyrolysis reaction of PCBs, WCC, AC and their mixing samples. The effect of adding coal powder to the pyrolysis gas product is

**Table 3**

Kinetics parameters of pyrolysis for samples.

Sample no.	Temperature range (°C)	Reaction order $n$	Pre-exponential factor $A$ ( $\text{min}^{-1}$ )	$E$ ( $\text{J mol}^{-1}$ )	Correlation coefficient $R$
1	>200	1.50	$3.09 \times 10^{17}$	$2.05 \times 10^5$	0.9936
2	>200	1.80	$1.00 \times 10^{18}$	$2.13 \times 10^5$	0.9938
3	>200	2.22	$3.47 \times 10^{14}$	$1.75 \times 10^5$	0.9916
4	200–1000	1.35	$1.94 \times 10^5$	$6.97 \times 10^4$	0.9953
	>1000	1.67	$6.32 \times 10^7$	$2.30 \times 10^5$	0.9690
5	200–450	1.90	$4.34 \times 10^{14}$	$1.76 \times 10^5$	0.9907
	450–850	1.03	66.50	$4.24 \times 10^4$	0.9822
	>850	1.35	$1.94 \times 10^5$	$1.65 \times 10^5$	0.9682
6	200–460	1.80	$3.41 \times 10^{12}$	$1.48 \times 10^5$	0.9985
	>460	1.50	0.3095	$1.96 \times 10^4$	0.9630
7	200–500	1.60	$5.16 \times 10^9$	$1.16 \times 10^5$	0.9967
	>500	1.33	$1.76 \times 10^5$	$1.61 \times 10^5$	0.9787
8	200–480	1.32	$2.90 \times 10^7$	$9.18 \times 10^4$	0.9916
	480–900	1.44	$1.29 \times 10^4$	$8.47 \times 10^4$	0.9734
	>900	1.50	$2.35 \times 10^6$	$1.90 \times 10^5$	0.9723
9	200–450	1	$5.91 \times 10^5$	$7.23 \times 10^4$	0.9953
	450–1000	1.55	$5.38 \times 10^2$	$6.27 \times 10^4$	0.9642
	>1000	1.35	$8.94 \times 10^6$	$2.09 \times 10^5$	0.9732
10	200–900	1.12	31.80	$3.67 \times 10^4$	0.9908
	>900	1.12	$9.74 \times 10^4$	$1.62 \times 10^5$	0.9606
11	>200	1.11	2.224	$3.01 \times 10^4$	0.9789

**Fig. 4.** FTIR spectrum for pyrolysis gas of no. 1 sample.**Fig. 6.** FTIR spectrum for pyrolysis gas of no. 8 sample.**Fig. 5.** FTIR spectrum for pyrolysis gas of no. 4 sample.**Fig. 7.** FTIR spectrum for pyrolysis gas of no. 10 sample.

discussed. Figs. 4–8 are the FTIR spectrum of gas evaporated in the pyrolysis of the Nos. 1, 4, 8, 10 and 11 samples, respectively.

The analytical results show that the gas product mainly consists of  $\text{CO}_2$ ,  $\text{CO}$  (the absorption peak of  $2150\text{--}2400\text{ cm}^{-1}$ ) and  $\text{H}_2\text{O}$  (the absorption peak of  $3400\text{--}3700\text{ cm}^{-1}$  and  $1500\text{--}1700\text{ cm}^{-1}$ ). In

addition, there is an asymmetric stretching vibration of methyl at  $1400\text{--}1600\text{ cm}^{-1}$  for the PCBs sample. The vibration peak of  $\text{C}\text{--}\text{C}$  exists at  $740\text{--}760\text{ cm}^{-1}$ . The  $\text{C}\text{--}\text{Br}$  characteristic absorption peak at  $520\text{--}540\text{ cm}^{-1}$  clearly appears at 300 and 400 °C for the PCBs



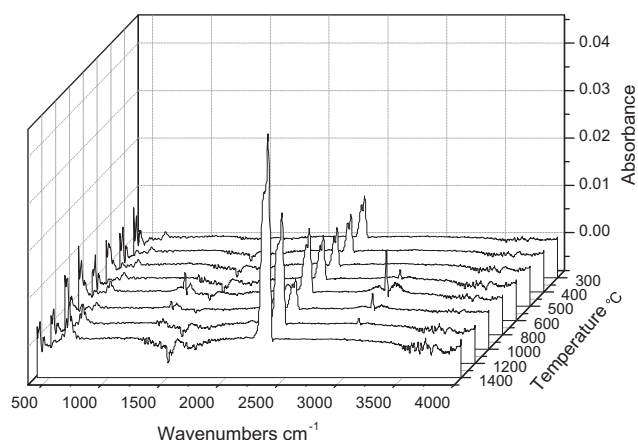


Fig. 8. FTIR spectrum for pyrolysis gas of no. 11 sample.

sample. The HBr characteristic absorption peak at  $2500\text{--}2750\text{ cm}^{-1}$  appears obviously at 300 and 400 °C for the PCBs sample. This is consistent with the results reported by Peng et al., 2006. There is no evident characteristic absorption peak of bromine for the mixed sample of PCBs and coal powder. It illustrates that there is no gas of hydrogen bromide or other bromide evaporated during the pyrolysis of the PCBs samples adding 40% coal powder. The adding coal powder probably plays a role of solidification effect on Br during the pyrolysis process of PCBs and make Br remain on the residues.

#### 4. Conclusions

The pyrolysis properties of the mixing samples are probably the results of interaction of PCBs and coal powder. The degree of mix pyrolysis and the pyrolysis properties are much better than single pyrolysis of PCBs or coal powder, respectively. The pyrolysis properties of mixing samples depend on the coal powder proportion and the type of coal.

Under nitrogen atmosphere, the DTG curve of the PCBs is a single arduous peak. The TG and DTG curve of the PCBs mixing with coal powder move to the high-temperature zone with the increase of coal powder and the DTG peak also becomes wider. The parameters of pyrolysis such as the temperature of maximum weight loss rate, the final temperature of reaction are improved in some degree. These properties show that the pyrolysis of PCBs mainly reacts in the low-temperature zone.

The Coats–Redfern model was used to fit pyrolysis to an n-level reaction model. The single pyrolysis of PCBs or AC is one-step reaction, and the pyrolysis reaction of the WCC is in several steps. The pyrolysis processes of other mixed samples have two or three reaction steps, the reaction orders are most in the range of 1–2, and the PCBs plays a leading role in pyrolysis of the mixing samples.

The FTIR analysis show that the gas product mainly consists of  $\text{CO}_2$ , CO and  $\text{H}_2\text{O}$ . The hydrogen bromide is mainly released at the fast weight-losing stage of PCBs sample. There is no evident characteristic absorption peak of bromine for the mixing sample of PCBs and coal powder. It illustrates that there is no gas of bromine or a bromine compound evaporated during the pyrolysis of the PCBs samples adding 40% coal powder. The adding coal powder probably solidifies the bromine in the residues during the pyrolysis process of PCBs.

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